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Analysis of 2H-Evaporator Scale Pot Bottom Sample [HTF-13-11-28H]

L. N. Oji

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REVIEWS AND APPROVALS

AUTHOR:

L. N. Oji, Author, Advanced Characterization & Processing Date

TECHNICAL REVIEW:

C. J. Martino, Advanced Characterization & Processing Date

APPROVALS:

F. M. Pennebaker, Manager, Advanced Characterization & Processing Date

S. L. Marra, Manager, Date
Environmental & Chemical Process Technology Research Programs

D. J. Martin, Manager, SRR PM-E-E-TFE Date

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EXECUTIVE SUMMARY

Savannah River Remediation (SRR) is planning to remove a buildup of sodium aluminosilicate scale from the 2H-evaporator pot by loading and soaking the pot with heated 1.5 M nitric acid solution. Sampling and analysis of the scale material from the 2H evaporator has been performed so that the evaporator can be chemically cleaned beginning July of 2013. Historically, since the operation of the Defense Waste Processing Facility (DWPF), silicon in the DWPF recycle stream combines with aluminum in the typical tank farm supernate to form sodium aluminosilicate scale mineral deposits in the 2H-evaporator pot and gravity drain line.

The 2H-evaporator scale samples analyzed by Savannah River National Laboratory (SRNL) came from the bottom cone sections of the 2H-evaporator pot. The sample holder from the 2H-evaporator wall was virtually empty and was not included in the analysis. It is worth noting that after the delivery of these 2H-evaporator scale samples to SRNL for the analyses, the plant customer determined that the 2H evaporator could be operated for additional period prior to requiring cleaning. Therefore, there was no need for expedited sample analysis as was presented in the Technical Task Request. However, a second set of 2H evaporator scale samples were expected in May of 2013, which would need expedited sample analysis.

X-ray diffraction analysis (XRD) confirmed the bottom cone section sample from the 2H-evaporator pot consisted of nitrated cancrinite, (a crystalline sodium aluminosilicate solid), clarkeite and uranium oxide. There were also mercury compound XRD peaks which could not be matched and further X-ray fluorescence (XRF) analysis of the sample confirmed the existence of elemental mercury or mercuric oxide.

On "as received" basis, the scale contained an average of 7.09E+00 wt % total uranium (n = 3; st.dev. = *8.31E-01* wt %) with a U-235 enrichment of 5.80E-01 % (n = 3; st.dev. = 3.96E-02 %). The measured U-238 concentration was 7.05E+00 wt % (n=3, st. dev. = *8.25E-01* wt %).

Analyses results for Pu-238 and Pu-239, and Pu-241 are 7.06E-05 ± *7.63E-06* wt %, 9.45E-04 ± *3.52E-05* wt %, and <2.24E-06 wt %, respectively. These results are provided so that SRR can calculate the equivalent uranium-235 concentrations for the NCSA. Because this 2H evaporator pot bottom scale sample contained a significant amount of elemental mercury (11.7 wt % average), it is recommended that analysis for mercury be included in future Technical Task Requests on 2H evaporator sample analysis at SRNL.

Results confirm that the uranium contained in the scale remains depleted with respect to natural uranium. SRNL did not calculate an equivalent U-235 enrichment, which takes into account other fissionable isotopes U-233, Pu-239 and Pu-241.

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LIST OF ABBREVIATIONS

CVAA-Hg	Cold Vapor Mercury by Atomic Absorption
DWPF	Defense Waste Processing Facility
HLW	High-Level Waste
ICP-ES	Inductively Coupled Plasma–Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
LSC	Liquid Scintillation Counting
NCSA	Nuclear Criticality Safety Assessment
PHA	Pulse Height Analysis
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TTA	Thenoyltrifluoroacetone
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
TTR	Technical Task Request

1.0 Introduction

Savannah River Remediation (SRR) is planning to remove a buildup of sodium aluminosilicate scale from the 2H-evaporator pot by the addition of dilute nitric acid solution[1]. 2H evaporator scale samples were obtained for characterization and dissolutions studies prior to the initiation of the cleaning process around July 2013. A separate set of 2H evaporator scale samples, to be used for Nuclear Criticality Safety Assessment (NCSA), will be obtained once the evaporator is shut down for cleaning.

Two scale samples (HTF-13-10-28H evaporator wall scrape sample and HTF-13-11-28H evaporator pot bottom sample) were pulled by SRR and delivered to Savannah River National Laboratory (SRNL) in January 2013 for analysis for primary fissile isotopes and non-fissile isotopes of uranium. However, when the evaporator wall scrape sample container (Sample HTF-13-10-28H) was opened in the shielded cell it was empty.

The 242-16H evaporator (2H evaporator) system concentrates high level waste consisting primarily of high-level waste (HLW) recycled to the SRS H-Area Tank Farm from the Defense Waste Processing Facility (DWPF). Historically, since the operation of DWPF, silicon in the recycle stream reacts with aluminum in the typical HLW to form sodium aluminosilicate mineral scale deposits in the evaporator pot and gravity drain line. The deposits are primarily nitrated sodium aluminosilicates with smaller amounts of clarkeite, Na((UO2)O(OH)). Nominally, the uranium in the scale is depleted in U-235 because the feed to the evaporator is depleted in U-235. In support of the criticality analysis, SRR obtained samples of evaporator scale from two different locations within the evaporator pot. SRR has requested that SRNL dissolve and analyze these samples for uranium and plutonium isotopic content and major radionuclide components. Crystallographic information for the samples was also requested.

The Technical Task Request (TTR) [1] and the Task Technical and Quality Assurance Plan [2] define the tasks and requirements for the performance of this characterization program by SRNL. This report contains the analytical results for the uranium isotopes, plutonium isotopes, other radionuclide analyses and crystallography for the 2H-evaporator pot scale sample. It is worth noting that after the delivery of these 2H-evaporator scale samples to SRNL for the analyses described above, the plant customer determined that the 2H evaporator could be operated for additional period prior to requiring cleaning. So therefore, there was no need for expedited sample analysis as was presented in the Technical Task Request. However, a second set of 2H evaporator scale samples is expected in May of 2013, which will need expedited sample analysis.

Although the TTR for this task did not call for elemental constituents and mercury analyses by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-ES) and CVHg, respectively, these analyses were included in the characterizations to satisfy environmental compliance requirements for this program.

2.0 Samples

On January 28, 2013, SRR sampled scale material from two locations in the 2H-evaporator pot and delivered the samples to SRNL. Figure 1A shows a picture of the scale material (HTF-13-11-28H evaporator pot bottom sample) contained in a weighing pan in the shielded cell after removal of the material from the original sampler. Weight of the “as-received” material was approximately 22 g. Figure 1B shows a picture of the wall scale material container (sample HTF-13-10-28H) which turned out to be virtually empty when it was opened in the shielded cell (No measurable amount of wall scale sample was found inside the sample holder).

3.0 Experimental Procedure

Three portions of the evaporator pot scale “as-received” sample (0.394 ± 0.030 g of the material in 100 mL dissolution volume giving an average digestion factor of 253.8 mL/g) were dissolved in the SRNL shielded cells using the sodium peroxide fusion digestion method. Uranium isotope analysis on the dissolved and diluted samples was obtained by using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS). Plutonium isotopes Pu-238, Pu-239/240 and Pu-241 were measured on the dissolved and diluted samples by thenoyltrifluoroacetone (TTA) separation and alpha Pulse Height Analysis (PHA) and beta Liquid Scintillation Counting (LSC). Small portions (0.06 gram) of the original scale samples were analyzed by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) to determine the crystalline phases present as well as confirm the presence of elemental mercury. Aqua regia digestion was also performed on the “as-received” scale sample and the resulting solution analyzed for transition metals and mercury by ICP-ES and CVAA-Hg, respectively.

4.0 Results and Discussion

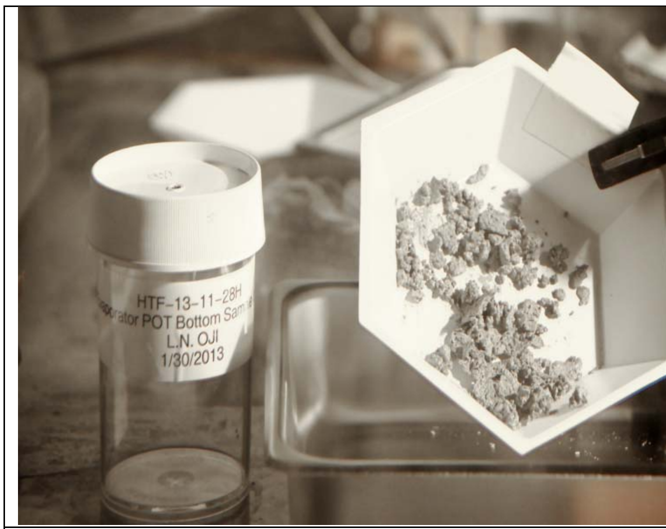
The XRD and XRF spectra for the 2H evaporator scale sample are presented in Figures 2 and 3, respectively. XRD analysis confirmed the bottom cone section sample, from the 2H-evaporator pot, consisted of clarkeite, uranium oxide and nitrated Cancrinite ($Na_{7.6}[AlSiO4)]_6(NO3)_{1.6}(H2O)_2$) [3]. There are mercury compound XRD peaks which could not be matched and further XRF analysis of the sample confirmed the existence of elemental mercury or mercuric oxide. The XRF spectra show that significant amount of mercury (average of 11.7 wt %) was found to be present in the sample relative to the uranium content.

Tables 1 and 2 contain the results for radionuclide and elemental constituent analysis for the 2H-evaporator pot scale sample. Analyses were performed in triplicate. A measure of uncertainty (±) as reported is the standard deviation of the multiple sample preparation analyses results. On “as received” basis, the scale contained an average of 7.09E+00 ± *8.31E-01* wt % total uranium. The U-235 enrichment, calculated as the U-235 concentration divided by total uranium concentration, was measured to be 5.80E-01 ± 3.96E-02 % The U-238 concentration is 7.05E+00 **±** *8.25E-01* wt %.

Analyses results for Pu-238 and Pu-239, and Pu-241 are 7.06E-05 **±** *7.63E-06* wt %, 6.81E-04 ± *9.82E-05 wt* %, and <2.24E-06 wt %, respectively. The Pu-241 analyses result, as presented, is an upper limit value. The Pu-239 data obtained by ICP-MS (9.45E-04 ± *3.52E-05 wt %)*, although about the same order of magnitude as the Pu-239/240 data, is significantly higher than the Pu-239/240 data which is based on another analytical method; Pu-ALPHA PHA method for Pu-239/240. One cannot assume that the Pu-239 by ICP-MS is all just Pu-239 because of expected spectral interferences as result of the presence of large U-238 peak which may overlap with the Pu-239 peak and the presence of interferences by uranium hydride peaks as well. Because of these interference possibilities, the Pu-239/240 value derived from Pu-ALPHA PHA method is considered more reliable and thus is the value reported in Table 1.

These results are provided so that SRR can calculate the equivalent uranium-235 concentrations for the NCSA.

Results for Al, Na and Hg are 8.34E+00 ± 6.76E-01, 1.01E+01 ± 7.25E-01and 1.17E+01 ±3.61E-01 wt %, respectively.



A: 2H-evaporator pot bottom (HTF-13-11-28H evaporator pot bottom sample). About 21.8 grams of sample extracted from sample holder

B: 2H-evaporator scale samples from the wall (HTF-13-10-28H evaporator wall scrape sample). Sample holder was virtually empty.

Figure 1 2H-evaporator pot bottom scale sample (insert A) and 2H-evaporator Wall scale sample container (insert B) [No measurable sample in container].

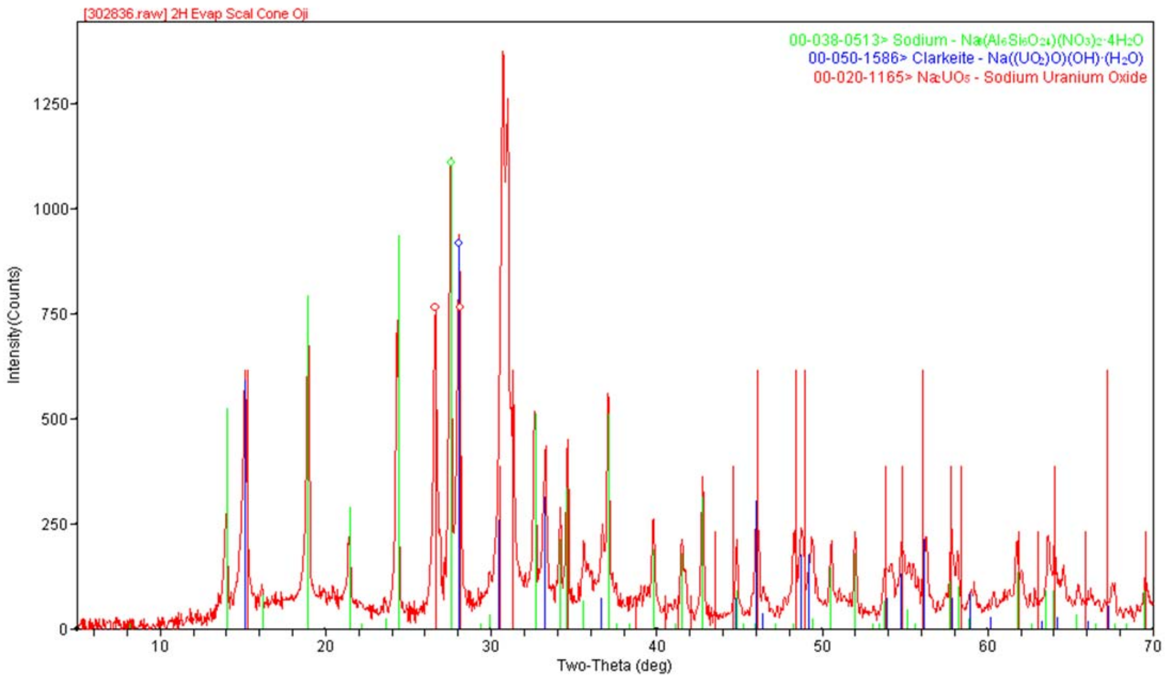


Figure 2 A. XRD analysis spectra result for 2H-evaporator pot bottom scale sample

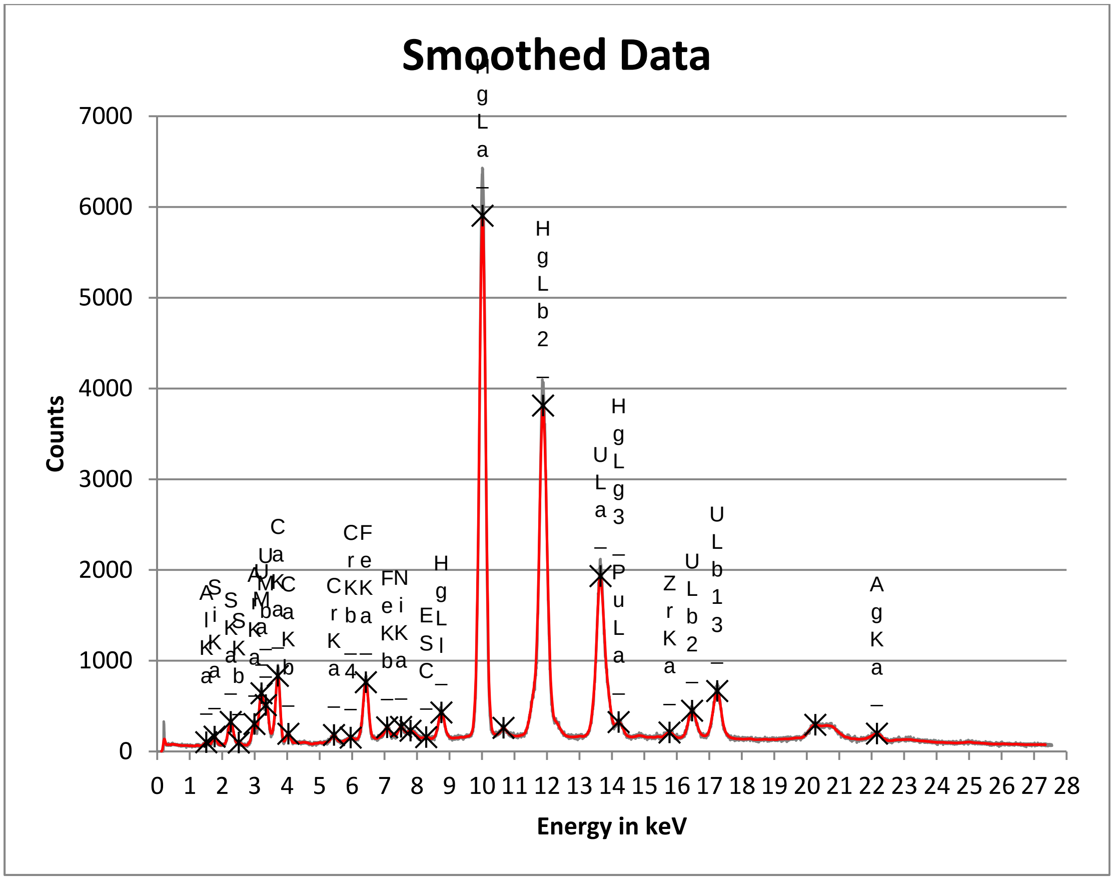


Figure 3 XRF analysis spectra result for 2H-evaporator pot bottom scale sample.

Table 1 Analysis of the 2H-Evaporator Pot Bottom Scale, HTF-13-11-28H

Analyte	**Preparation 1,**	**Preparation 2**	**Preparation 3**	**Average,**	**St.dev.**	**Units**
Cs-137	5.79E+07	6.05E+07	5.84E+07	**5.89E+07**	*1.38E+06*	dpm/g
Ba-137m	5.48E+07	5.72E+07	5.52E+07	**5.58E+07**	*1.31E+06*	dpm/g
Co-60	6.49E-10	6.29E-10	7.01E-10	**6.60E-10**	3.70E-11	wt %
Sr-90	1.82E-03	1.82E-03	2.32E-03	**1.99E-03**	2.92E-04	wt %
Y-90	4.57E-07	4.55E-07	5.83E-07	**4.98E-07**	7.31E-08	wt %
Sb-125	<5.33E-09	<4.71E-09	<3.77E-09	**<4.60E-09**		wt %
Ce-144	<8.33E-09	<7.44E-09	<7.74E-09	**<7.84E-09**		wt %
Eu-154	3.52E-08	3.87E-08	4.04E-08	**3.81E-08**	2.64E-09	wt %
Cm-242	1.40E-11	1.66E-11	1.69E-11	**1.59E-11**	1.58E-12	wt %
Cm-244	2.67E-07	3.60E-07	5.24E-07	**3.84E-07**	1.30E-07	wt %
Am-241	1.22E-05	1.51E-05	2.30E-05	**1.67E-05**	5.59E-06	wt %
Am-242m	5.75E-09	6.81E-09	6.95E-09	**6.50E-09**	6.59E-10	wt %
Am-243	2.87E-06	5.54E-06	5.18E-06	**4.53E-06**	1.45E-06	wt %
Th-232	1.13E-02	1.09E-02	9.74E-03	**1.06E-02**	8.10E-04	wt %
U-233	3.96E-04	3.45E-04	4.96E-04	**4.12E-04**	7.68E-05	wt %
U-234	1.27E-03	1.03E-03	1.31E-03	**1.20E-03**	1.51E-04	wt %
U-235	4.35E-02	3.44E-02	4.56E-02	**4.12E-02**	5.95E-03	wt %
U-236	2.06E-03	2.08E-03	2.56E-03	**2.23E-03**	*2.83E-04*	wt %
U-238	6.94E+00	6.28E+00	7.92E+00	**7.05E+00**	*8.25E-01*	wt %
U-Total	6.99E+00	6.32E+00	7.97E+00	**7.09E+00**	*8.31E-01*	wt %
U-235/Total U*100	6.23E-01	5.44E-01	5.72E-01	**5.80E-01**	3.96E-02	%
Np-237	1.00E-03	8.74E-04	1.09E-03	**9.88E-04**	*1.08E-04*	wt %
Pu-238	7.08E-05	6.29E-05	7.81E-05	**7.06E-05**	*7.63E-06*	wt %
Pu-241	<2.29E-06	<2.01E-06	<2.42E-06	**<2.24E-06**		wt %
Pu-239/240*	7.01E-04	5.75E-04	7.68E-04	**6.81E-04**	*9.82E-05*	wt %
Pu-239 (ICP-MS)	9.16E-04	9.34E-04	9.84E-04	**9.45E-04**	*3.52E-05*	wt %

***The Pu-239 data alone, obtained by ICP-MS, is higher than the Pu-239/240 data based on Pu-ALPHA PHA method for Pu-239/240. Spectral interferences are a possible source of significantly larger ICP-MS values for Pu-239.**

Table 2 Elemental Constituents of 2H-Evaporator Pot Bottom Scale Sample

Analytical Component	Preparation 1, wt %	Preparation 2 wt %	Preparation 3 wt %	Average, wt %	St. dev.
Ag	<9.83E-03	<1.11E-02	<9.69E-03	**<1.02E-02**	
Al	7.98E+00	9.12E+00	7.92E+00	**8.34E+00**	*6.76E-01*
B	3.83E-03	3.87E-03	3.75E-03	**3.82E-03**	*6.11E-05*
Ba	3.39E-03	3.19E-03	3.03E-03	**3.20E-03**	*1.80E-04*
Be	<6.82E-05	<7.69E-05	<6.72E-05	**<7.08E-05**	
Ca	1.80E-01	1.75E-01	1.70E-01	**1.75E-01**	*5.00E-03*
Cd	<4.77E-03	<5.38E-03	<4.71E-03	**<4.95E-03**	
Ce	<4.65E-02	<5.25E-02	<4.59E-02	**<4.83E-02**	
Co	<1.05E-02	<1.19E-02	<1.04E-02	**<1.09E-02**	
Cr	2.76E-03	3.68E-03	5.90E-02	**2.18E-02**	*3.22E-02*
Cu	<5.57E-03	<6.28E-03	<5.49E-03	**<5.78E-03**	
Fe	1.79E-01	2.07E-01	3.80E-01	**2.55E-01**	*1.09E-01*
Gd	1.72E-02	1.63E-02	1.49E-02	**1.61E-02**	*1.16E-03*
K	<1.35E-02	<1.52E-02	<1.33E-02	**<1.40E-02**	
La	<7.16E-03	<8.08E-03	<7.06E-03	**<7.43E-03**	
Li	2.01E-03	2.04E-03	1.94E-03	**2.00E-03**	*5.13E-05*
Mg	1.04E-03	1.29E-03	8.85E-04	**1.07E-03**	*2.04E-04*
Mn	1.16E-02	1.30E-02	1.58E-02	**1.35E-02**	*2.14E-03*
Mo	<5.59E-03	<6.30E-03	<6.40E-03	**<6.10E-03**	
Na	9.75E+00	1.09E+01	9.56E+00	**1.01E+01**	*7.25E-01*
Ni	2.82E-02	2.64E-02	5.60E-02	**3.69E-02**	*1.66E-02*
P	<9.46E-03	<1.07E-02	<9.33E-03	**<9.83E-03**	
Pb	<4.65E-03	<5.24E-03	<4.58E-03	**<4.82E-03**	
S	<3.41E-01	<3.85E-01	<3.36E-01	**<3.54E-01**	
Sb	<1.12E-01	<1.27E-01	<1.11E-01	**<1.17E-01**	
Sn	<6.72E-03	<7.58E-03	<6.62E-03	**<6.97E-03**	
Sr	1.04E-02	9.58E-03	9.29E-03	**9.76E-03**	*5.76E-04*
Th	<7.30E-02	<8.23E-02	<7.19E-02	**<7.57E-02**	
Ti	<8.75E-03	<9.87E-03	<8.63E-03	**<9.08E-03**	
U	7.03E+00	6.59E+00	6.31E+00	**6.64E+00**	*3.63E-01*
V	<3.58E-04	<4.04E-04	<3.53E-04	**<3.72E-04**	
Zn	2.39E-03	2.10E-03	1.85E-03	**2.11E-03**	*2.70E-04*
Zr	<4.77E-03	<5.38E-03	<4.71E-03	**<4.95E-03**	
Hg	1.16E+01	1.21E+01	1.14E+01	**1.17E+01**	*3.61E-01*

5.0 Conclusions

The evaporator pot bottom scale sample (HTF-13-11-28H) are composed of nitrated cancrinite (a crystalline sodium aluminosilicate solid), and clarkeite (a uranium oxy-hydroxide) and sodium uranium oxide. Because the 2H evaporator pot bottom scale sample contained a significant amount of elemental mercury (averaging 11.7 wt %), it is recommended that analysis for mercury be included in future Technical Task Requests on 2H evaporator sample analysis at SRNL.

Results confirm that the uranium contained in the scale remains depleted with respect to natural uranium. SRNL did not calculate an equivalent U-235 enrichment, which takes into account other fissionable isotopes U-233, Pu-239 and Pu-241.

6.0 Quality Assurance

This work was performed in accordance with the requirements of the task technical request. The experimental data are for these analyses are contained in Laboratory Notebook SRNL-NB-2011-00089 and various Analytical Development (AD) notebooks. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

7.0 References

1. H. Bui, “2H Evaporator Scale Sampling Analysis,” X-TTR-H-00021, Rev. 0, January 16, 2013.

2. L N. Oji, “Task Technical and Quality Assurance Plan for 2H Evaporator Scale Sample Analysis and Dissolution Studies” SRNL-RP-2013-00033, Rev. 0, January 18, 2013.

3. J. C. Buhl. F. Stief, M. Fechtelkord, T. M. Gesing, U. Taphorn, and C. Taake, “Synthesis, X-ray diffraction and MAS NMR characteristics of nitrate cancrinite Na7.6[AlSiO4]6(NO3)1.6(H2O)2,” Journal of Alloys and Compounds, 305, 93-102, (2000).

4. K. B. Martin and C. J. Martino, “The 2H Evaporator Pot & Gravity Drain Line Scale Nuclear Criticality Analysis Suite,” WSRC-STI-2008-00185, Rev. 0, April 21, 2008.

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